

## **APPENDIX C**

**Standard Method Used At  
Pacific Northwest National Laboratory  
For Measuring Laboratory Batch  $K_d$  Values**

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### **Standard Method Used At Pacific Northwest National Laboratory For Measuring Laboratory Batch $K_d$ Values**

*The standard method reproduced below is used by the authors of this report and their coworkers at the Pacific Northwest National Laboratory in Richland, Washington for the measurement of  $K_d$  values. It is adapted from the procedure described in Relyea et al. (1980).<sup>1</sup>*

#### 1.0 Applicability

This procedure describes the method for measuring radionuclide distribution coefficients ( $K_d$ 's) of geologic material. This procedure includes descriptions for analyses of unconsolidated, loosely consolidated, consolidated porous, and intact, impermeable geological materials.

#### 2.0 Definitions

- Cold wash: Contact of solid sample with nonradioactive groundwater for purposes of establishing chemical equilibrium with nontracer aqueous constituents.
- Tracer: Radioactive element added to groundwater solution to indicate migration and retardation events.
- Spiked groundwater: Groundwater with tracer.
- Blank tube: Centrifuge tube containing spiked groundwater but no solids.
- Radiation Work Procedure (RWP): This is a set of instructions for safe handling of radioactive material in the laboratory. The RWP covers a number of topics and shall be read and understood before performing any work in the laboratory.

#### 3.0 Responsible Staff

- Task leader
- Cognizant staff

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<sup>1</sup> Relyea, J. F., R. J. Serne, and D. Rai. 1980. *Methods for Determining Radionuclide Retardation Factors: Status Report*. Pacific Northwest Laboratory, Richland, Washington

## 4.0 Procedure

### 4.1 Materials

pH meter  
pH combination electrode 0-14 pH  
Magnetic stirrer  
Stir bars  
Scintillation vials  
pH buffers  
Groundwater  
No. 18 stainless steel sieve (1 mm)  
No. 50 sieve (0.3 mm)  
Mortar and pestle  
Analytical balance (accuracy within  $\pm 0.01$  g) - Refer to operation manual specific to balance for use instructions.  
50 ml polycarbonate centrifuge tubes with screw caps  
Teflon tape  
Groundwater  
Orbit shaker  
Centrifuge  
Vacuum pipets  
0.45-micrometer polycarbonate membrane filters  
Radioactive tracer  
Plastic bags

### 4.2 Safety Precautions

In using radioactive substances and/or solutions protective clothing should be used to reduce the possibility of contamination. Each laboratory is supplied with a radiation work procedure (RWP) which outlines the types and quantities of radionuclides permitted with instructions for handling. Record the number of the RWP in the laboratory record book.

### 4.3 Sample Characterization

Before the  $K_d$  study perform the following analyses to characterize solid and groundwater samples (perform groundwater analysis within one month prior to study). Include the following:

#### 4.3.1 For groundwater

- pH
- bulk chemistry (Ca, Mg, Na, K, Cl, NO<sub>3</sub>, SO<sub>4</sub>, CO<sub>3</sub>, HCO<sub>3</sub>)

#### 4.3.2 For solids

- Mineralogy
- Surface area
- Cation exchange capacity
- Moisture content
- Particle size analysis

Procedures which may be used to determine the above parameters are referenced at the end of this document. Record all results.

### 4.4 Sample Preparation

#### 4.4.1 Groundwater

- 4.4.1.1 Filter groundwater through a 0.45- $\mu$ m polycarbonate membrane before it is used in a batch K<sub>d</sub> measurement.
- 4.4.1.2 If retardation parameters (such as pH, ionic strength, and complexing ligand concentration) are to be studied, chemically analyze the synthetic or altered groundwater after preparation and filtration and record results.

#### 4.4.2 Solid

- 4.4.2.1 Unconsolidated Material. To remove particles greater than one millimeter (>1.0 mm), the sample shall be wet-sieved with groundwater by passing the sample through a No. 18 stainless steel sieve. If tests with the material are to be conducted in an inert atmosphere or in a controlled atmosphere, rock samples are to be prepared under those same atmospheric conditions. This requires minimum contact of the rock with air from the time it is removed from the earth until the time the experiment is concluded. This condition holds for Sections 4.5.2.2 and 4.5.2.3. The particle size shall be determined and reported with results from Section 4.3.
- 4.4.2.2 Loosely Consolidated Material. The sample shall be disaggregated by an ultrasonic method or by hand with a mortar and pestle. A portion of the intact material shall be preserved for dynamic testing. Disaggregation

shall proceed no farther than that required to reduce the sample to its natural grain size. Fresh surfaces will be exposed to weathering, but this procedure should reduce fracturing of particles to a minimum. Remove particles >1.0 mm as in Section 4.5.2.1. The particle size distribution after disaggregation shall be reported with results in Section 4.3.

- 4.4.2.3 Consolidated Porous Material (and intact, impermeable rock). A portion of the intact sample shall be preserved (and maintained under conditions that simulate those in situ) for dynamic testing. The remaining sample is to be crushed to pass through a No. 18 sieve (<1 mm). Crushing must be accomplished by means that minimize the introduction of extraneous material, such as metal filings, into the sample. The sample should then be wet sieved through a No. 50 sieve (0.30 mm) to obtain particle sizes between 0.30 mm and 1.00 mm.
- 4.4.2.4 After samples have been sized (Sections 4.5.2.1, 4.5.2.2 or 4.5.2.3), they must be homogenized to insure that the same particle size distribution is obtained for each subsample to be studied.

#### 4.4.3 Equilibrium

- 4.4.3.1 Prepare 50 ml polycarbonate centrifuge tubes with screw caps by obtaining and recording tare weights and assigning identifications which are unique to each sample tube.
- 4.4.3.2 After homogenizing, 1-g ( $1.0 \text{ g} \pm 0.01 \text{ g}$ ) samples are to be weighed (and weights recorded) into centrifuge tubes. Wrap centrifuge tube threads with Teflon tape to prevent leaks.
- 4.4.3.3 Thirty-milliliters of filtered, nonspiked (no radioactive tracer) groundwater is added to each tube, including blanks with no soil, for a “cold” wash. The tube caps are to be replaced before the tubes are placed on a shaker for a gentle overnight agitation (about one oscillation per second).
- 4.4.3.4 Next centrifuge the tubes to separate solids and liquids. Remove the solutions with a vacuum pipettes to prevent removal of the rock sample (some liquid will remain in the tube).
- 4.4.3.5 Repeat the wash procedure twice more for a total of three cold (nonradioactive) washes. Before the centrifuge step on the third wash, measure and record the pH of the solid-solution. If the pH has changed from its natural equilibrium value as measured in the field, the rock

sample and groundwater have not yet re-established equilibrium. Continue to wash until the pH is stable. A change in pH is most likely to occur with samples of crushed rock (Section 4.4.2.3) because fresh surfaces (either rock or cementing agents) have been exposed.

- 4.4.4 After removal of the third wash solution, each tube must be reweighed and the weight must be recorded to determine the volume of excess solution left in each sample. Secure the cap of each tube to prevent evaporation, which would result in an increased salt concentration in the remaining solution. The excess solution volume is found by dividing the excess solution weight by the solution density.

## 4.5 Addition of Tracer

- 4.5.1 The adding of tracer to a solution represents a critical step in the execution of radionuclide migration studies. Two items must be carefully considered: (1) the total amount of tracer added must be soluble in the volume of solution used and (2) the chemical composition of the groundwater or synthetic groundwater must remain unchanged, except for the addition of the radionuclide(s) to be studied.
- 4.5.2 Dry the tracers so that excess acid or base in the stock solution is removed. Do not dry volatile tracers in acid media or they will be lost. The chemical produced by drying must be soluble in the solutions used in experimentation. (An incorrect procedure would be to dry plutonium basic media that would produce an insoluble  $\text{PuO}_2$  or  $\text{Pu}[\text{OH}]_4$  precipitate.)
- 4.5.3 Exception to the dry-addition rule must be made in some cases for radionuclides that have multiple oxidation states. When drying might change the tracer stock solution's oxidation state--such as  $\text{Pu(VI)}$  to  $\text{Pu(IV)}$ --tracer should be added to solution in as small a volume as possible with as little excess salt and acid or base as possible. Otherwise, a dry, soluble, salt-free tracer shall be added to groundwater.
- 4.5.4 Allow the tracer solution to sit for at least one week under conditions to be used in the experiment (in equilibrium with air if the aquifer is in equilibrium with air, or under controlled atmosphere conditions if the aquifer is not in equilibrium with air). Make any necessary adjustments to pH during the equilibration time. Solution is to be filtered ( $0.45\ \mu\text{m}$ ) after equilibration prior to contact with the geologic material.
- 4.5.5 Calculate and record the amount of tracer (mol/l) present in the groundwater just prior to contact with the geologic material. Additionally, report any carrier isotope of the element added with the tracer and any natural occurrence of the element in groundwater.

## 4.6 Rock and Groundwater Contact

- 4.6.1 Thirty milliliters (30 ml) of filtered groundwater containing the radioactive tracer is added to each sample tube containing one gram (1 g) of solid. In addition, 30 ml of spiked groundwater is placed in each of three empty (blank) centrifuge tubes (prewashed as in Section 4.4.3). The blank tubes are needed to detect sorption of tracer by centrifuge tube walls.
- 4.6.2 After replacing the tube caps, the tubes are placed in plastic bags (5 to 20 tubes per bag) to contain any contamination caused by leaky tubes. Next, the tubes are placed on a shaker (for linear reciprocating shaker, place tubes horizontally) so that the solid-solution mixture makes maximum contact. Set the shaking speed to 0.8 to 1.2 oscillations per second to ensure mixing of solid and liquid but to reduce grinding of particles.
- 4.6.3 If time is not a parameter being studied, then contact between solid and liquid is to be seven days (7 days). Record the actual contact time allowed. The samples are then removed from the shaker and the tubes are visually checked for leaks (decontaminate if necessary and discard leaky tubes).
- 4.6.4 The blank and sample tubes are centrifuged for twenty minutes (20 min) at 10,000 g ( $g = 980 \text{ cm/sec}^2$ ) or more, and fifteen milliliters (15 ml) of effluent is filtered through a pre-washed  $0.45 \mu\text{m}$  polycarbonate-membrane-type filter. (Pre-wash with groundwater from Section 2.2 to remove foreign particles and soluble impurities). Analyze filtered effluent samples for tracer activity. Next, the effluent is decanted from the blanks into cleanly washed tubes and the empty blank tubes are analyzed for tracer activity adsorbed on tube walls. If tracer activity on blank tube walls is greater than 10 percent of the total blank activity (determined in Section 4.7.3), do not use the blank influent activity for  $K_d$  calculation. If the activity sorbed on blank walls is significantly greater than 10 percent (using a one-tailed “t” test and combined counting error and statistical variation between blanks), directly count the activity of the sample. Methods for both cases follow.

## 5.0 Batch $K_d$ Calculations

### 5.1 When tracer is not sorbed by blank tube wall

- 5.1.1 Data needed for  $K_d$  calculation are: (1) excess solution volume,  $V_{\text{excess}}$ , (ml) left from the third cold wash (weight of excess solution divided by solution density); (2) mass of solid aquifer material,  $M_{\text{sed}}$ , (g); (3) volume of groundwater with radioactive tracer added,  $V_{\text{spike}}$  (ml); (4) activity or concentration of tracer in the

effluent solution,  $C_{\text{effluent}}$  (dpm/ml); and (5) the tracer activity or concentration in the influent blank,  $C_{\text{blank}}$ , (dpm/ml).

5.1.2 The tracer concentration on the solid phase,  $A_i$  (or  $q_i$ ), is:

$$A_i = q_i = \frac{(C_{\text{blank}} \times V_{\text{spike}}) - C_{\text{effluent}}(V_{\text{spike}} + V_{\text{excess}})}{M_{\text{sed}}} \quad (1)$$

The  $K_d$  is then given by:

$$K_d = \frac{(C_{\text{blank}} \times V_{\text{spike}}) - C_{\text{effluent}}(V_{\text{spike}} + V_{\text{excess}})}{C_{\text{effluent}} \times M_{\text{sed}}} \quad (2)$$

## 5.2 When tracer is sorbed by blank tube wall (Gamma or X-ray Emitting Isotopes)

5.2.1 If the radioactive tracer is adsorbed on the walls of blank tubes, determine the tracer adsorbed by the solid by direct measurement. Use a traceable standard made with the same type of geologic material as used in the test.

5.2.2 For this procedure, after the sediment and traced groundwater have contacted for at least 7 days, the samples are centrifuged to separate solids from liquids, then the liquid effluent is decanted from the sample tube using a vacuum pipette, and the sample is weighed to determine the excess effluent solution volume ( $V_{\text{excess}}$ ). The solid sample is then dried (it should be “air dried” in the same manner as when originally weighed, either in air or in a controlled atmosphere) and transferred to a clean polycarbonate centrifuge tube. The weight of the dry sample  $M_{\text{sed}}$  (g) is then determined and radiocounting of the dry sample is performed for tracer activity,  $C$  (dpm), using the same detector, sample position, and radioanalytical techniques as used for the attenuation standard prepared in Section 5.2.1.

5.2.3 Determine the effluent tracer activity,  $C_{\text{effluent}}$  (dpm/ml), in geometries that are traceable to a standard. The  $K_d$  can then be calculated from:

$$K_d = \frac{C - (C_{\text{effluent}} \times V_{\text{excess}})}{C_{\text{effluent}} \times M_{\text{sed}}} \quad (3)$$



### 5.3 When tracer is sorbed by blank tube wall ( $\alpha$ - or $\beta$ -Emitting Isotopes)

- 5.3.1 If the radioactive tracer is adsorbed by sample container walls, only the effluent activity can be determined simply and directly. Two options are available for determination of the activity adsorbed by the rock sample. One method is to remove both the solid sample and effluent from the original container and to strip the isotope from the container wall by some means. Mass balance will allow calculation of the  $K_d$  if one knows the amount of radionuclide in the effluent on the tube wall and the total radionuclide initially added. A second method is to chemically remove the radionuclide from the rock sample and count it.

Problems with the first method include the possibility that some of the solid may adhere to the wall and raise the apparent activity of the nuclide adsorbed by the container. Removal of the solid sample may also cause leaching of the container wall and result in an apparent low activity for nuclides adsorbed by the container. This can be minimized by using tubes made of material most appropriate to your sample; consider Teflon, glass, or various plastics to minimize adherence.

The second method is subject to incomplete removal of the nuclide from the solid or loss of material during any additional steps required for extraction, or both.

## 6.0 Reporting Results from Radionuclide Migration Experiments

- 6.1 The following generic  $K_d$  coding form (Table 1) includes the information to be obtained. (The different data categories and abbreviations are described in Section 6.2.)

### 6.2 Explanation of $K_d$ Coding Form

#### 6.2.1 Category I. Reference

- A. *Name* of the person who performed experiments
- B. *Date* that the experiment was started.
- C. *Comments* regarding deviations from procedure, anomalies that occurred during the process, other pertinent information.

**Table 1.** Generic  $K_d$  coding form.

Reference	Experimental Details	Geologic Media	Aqueous Phase	Nuclide	Adsorption Function
A. Name	A. Method	A. Name	A. BEG	A. ISO	A. $K_d$
B. Date Started	B. State	B. Origin	B. Macro	B. CONC	B. Units
C. Comments	C. Ratio	C. Total	C. Trace	C. SPE	C. Direction
	D. Time	D. Mineral	D. END	D. ADD	D. NUM
	E. Temperature	E. $CO_3$		E. Loading	
	F. ATM	F. OX			
	G. SEP	G. CEC			
	H. Analyze	H. AEC			
	I. RAD	I. SA			

### 6.2.2 Category II. Experimental Details

- A. *Method* refers to batch, axial filter, column, intact core, channel chromatography, and so forth. For batch method, add more detail as to whether cold washes and blank corrections were used. For example, use mnemonics such as
- “BATCH (3W, BC) = batch, three cold washes, with blank tube sorption correction”
- “BATCH (OW) = batch, zero cold washes and no correction.”
- B. *State* of geologic media such as crushed 40  $\mu\text{m}$ ; intact core 2.5 cm dia x 5 cm; tablet 1 cm x 0.5 cm; crushed 30-80  $\mu\text{m}$ , etc.
- C. *Ratio* of solids to solution for batch  $K_d$ ; for columns include pore velocity or column velocity (for example, 1 PV = 1 cm/hr, CV = 0.5 cm/hr) and porosity and column bulk density; PR = porosity, BD = bulk density.
- D. *Time* of contact such as shaking time for batch system or residence time in flow through columns (h) = hours, (d) = days.

- E. *Temp* is the temperature of the experiment in °C.
- F. *ATM* is the equilibrating atmosphere air, N<sub>2</sub>, Ar, 10 percent CO<sub>2</sub> - 90 percent Ar, and so forth.
- G. *SEP* stands for separation technique; did you use filters (give median pore size) or centrifugation (include approximate g's)?  
  
 "FIL(.4) = filter 0.4 m"  
  
 "CEN(50) = centrifuged at 50 g's where g = 980 cm/sec<sup>2</sup> units."
- H. *Analyze* states whether the K<sub>d</sub> is determined by analyzing (or counting) liquids only or solid and liquid:  
  
 "L/L = liquids only"  
  
 "S/L = solid and liquid"
- I. *RAD* is a list of all radioisotopes that were run simultaneously in the experiment. Example: "Sr, Cs, Tc" means these isotopes were run together.

### 6.2.3 Category III. Geologic Media

- A. *Name*. Use the generic name of the rock or mineral, *e.g.*, basalt, granite, montmorillonite.
- B. *Origin*. Include a geographic description and some formation information, *e.g.*, Eleana shale, Sentinel Gap basalt, Argillaceous Shale Wards #404561.
- C. *Total*. Identify the chemical composition as oxides (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>TiO<sub>2</sub>, FeO, Fe<sub>2</sub>O<sub>3</sub>, MnO, CaO, MgO, K<sub>2</sub>O, Na<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub> in percent.
- D. *Minerals*. Identify the minerals present in the rock sample, listing the major ones first, the minor ones last, in the order of the composition percentages in which they appear (largest first). If there are quantitative estimates, add this information as percent and tr = 5 percent.
- E. *CO<sub>3</sub>* = carbonate content of rock.
- F. *OX* = hydrous Fe, Mn, Al oxides content of rock.

- G. *CEC* = cation exchange content of material; units = meq/100g. Specify pH of system (typically pH = 7).
- H. *AEC* = anion exchange content of material; units = meq/100g. Specify pH of system.
- I. *SA* = surface area; use “EG” for ethylene glycol, “BET” for gas adsorption, use units m<sup>2</sup>/g, for example: EG(1.3).

#### 6.2.4 Category IV. Aqueous Phase

- A. *BEG* signifies measurements made prior to tracer adsorption.
- B. *Macro* constituents include:
  - pH
  - Eh (units vs. S.H.E.)
  - Na<sup>+</sup>
  - Ca<sup>2+</sup>
  - K<sup>+</sup>
  - Mg<sup>2+</sup>
  - Cl<sup>-</sup>
  - HCO<sub>3</sub><sup>-</sup>; CO<sub>3</sub><sup>2-</sup>
  - SO<sub>4</sub><sup>2-</sup>
  - SiO<sub>4</sub>
- C. *Trace* constituents include:
  - NO<sub>3</sub>, ppm
  - Organic carbon
  - B
  - Trace metals or anything else measured.
- D. *END* signifies measurements (if performed) taken at the same time as K<sub>d</sub> determined.

#### 6.2.5 Category V. Nuclide

- A. *ISO*. Isotope used such as <sup>237</sup>Pu, <sup>95m</sup>Tc.
- B. *CONC*. Concentration added to groundwater in M = molarity. Include any carrier if present.

- C. *SPE*. Species or valence state added, if known. Also state whether the valence state distribution was determined after equilibration state, *e.g.*, “Pu(VI) BEG; Pu(IV) 15 percent, Pu(V) 50 percent, Pu(VI) 10 percent END” (which means that the original spike was 100 percent Pu(VI), and after shaking the final distribution was as shown).
- D. *ADD* describes how the tracer was added to the groundwater; DRY means evaporated to dryness and groundwater added; WET/PH/3DFO.4 means a small aliquot of liquid tracer was added to the groundwater, the pH of the system was re-adjusted to the appropriate value and shaken for 3 days to filtration through 0.4  $\mu\text{m}$  filters before usage.
- “DRY/1DC50” means the dried spike was brought back into solution equilibrated for one day, and centrifuged at 50 g’s before usage.
- E. *Loading* describes (a) the percent of total exchange capacity of the adsorbent filled with the nuclide of interest or (b) the mass of nuclide adsorbed/mass of adsorbent at the condition when the  $K_d$  measurement is performed. This value can be calculated from knowledge of the cation or anion exchange capacity in case (a) and from mass balance considerations. One must know the original mass of the nuclide used in each experiment.

#### 6.2.6 Category VI. Adsorption Function

- A.  $K_d$ . Place the value for  $K_d$ . If a retardation factor is determined in a flow-through column as a function of water velocity, designate by the symbol RF.

Where several measurements were made, also give the standard deviation, such as

“ $75 \pm 12 = a K_d$ ”

“(RF)  $60 \pm 30 = \text{retardation factor}$ ”

- B. *Units*. ml/g or ml/m<sup>2</sup>.
- C. *Direction*.      ADS = adsorption direction  
                              DES = desorption direction  
                              ADS-DES = A spike addition to a column.
- D. *NUM* = number of observations used to derive data point, for example:  
      3 = triplicate samples.